ON A CONSISTENCY TEST OF THE THEORIES OF STRONG ELECTROLYTES IN SOLUTION *

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ABSTRACT. In the original Debye Hückel theory the Poisson equation has been evaluated on the assumption that

$$e^{-\frac{\epsilon\psi}{kT}} = 1 - \frac{\epsilon\psi}{kT}, \text{ i.e. } \frac{\epsilon\psi}{kT} << 1$$

In this paper it has been shown that the value of $\frac{\epsilon\psi}{kT}$ with which the actual thermodynamic calculations have been made in the theory, is generally > 1. Thus at least in this respect the original calculations of Debye and Hückel are inconsistent. Incidentally, a similar test applied to the theory of Bagchi shows that this theory is generally consistent in this respect.

In the theory of strong electrolytes due to Debye and Hückel, (1923) the interionic field is assumed to satisfy the Poisson equation :

$$\Delta^2\psi = -\frac{4\pi}{D}\rho$$

where ρ is calculated by applying Boltzmann's distribution formula. In the general case, when the solution contains ions of different species 1, 2, ..., i, j, ..., s. the above reduces to :

$$\Delta^2\lambda_i = -\frac{4\pi\epsilon^2}{DkT}\sum_{j=1}^{s} n_j Z_j e^{-Z_j\lambda_i} \qquad \ldots \quad (1)$$

where,

ψ_i = electrostatic potential round any central ion of the i_{th} type

$$\lambda_i = \frac{\epsilon\psi_i}{kT}$$

n_i and Z_i are the number density and valence, respectively of the i^{th} sort of ions in solution, ϵ, D, k, and T have thier usual significance.

To facilitate the integration of the above partial differential equation (1), $\sum_{j=1}^{s} n_j z_j e^{-z_j\lambda_i}$ has been replaced by $-\sum_{j=1}^{s}(n_j z_j^2)\lambda_i$ on the assumption that

$$Z_j\lambda_i << 1 \qquad \ldots \quad (2)$$

The expression then obtained for λ_i as a function of the distance r from the central ion of charge Z_i is :

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$$\lambda_i = \frac{Z_i e^2 e^{Ka_i}}{DkT(1+Ka_i)} \cdot \frac{e^{-Kr}}{r} \qquad (3)$$

where,

$K^2 \quad \frac{4\pi\epsilon^2}{DkT} \sum_{j=1}^{i} n_j Z_j^2$ and

a_i = the average value of the distance upto which the surrounding ions can approach the central ion.

The additional free energy of the ions due to the interionic field which only is of real significance in the theory, is calculated from consideration of an ideal process of charging-discharging of the ions, or by other thermodynamic methods. However, it is significant that all these methods utilise only the value of the potential at the surfaces of the ions (really, the surfaces of the "Deckungssphären" of ions).

Now if contrary to the condition (2), it is found that $Z_j\lambda_i \geq 1$, then the higher powers of $Z_j\lambda_i$ in the exponential series become significantly large compared to $Z_j\lambda_i$, and cannot be neglected. Since, moreover, only the value of λ_i at $r=a_i$ is important, it is obvious that the consistency of the theory demands that $Z_j(\lambda_i)_{r=a_i} < 1$

This simple requirement of the theory has been tested here (Table I) by calculating $Z_j(\lambda_i)_a$ from equation (3) for different ions, at different concentrations (molar) and at 25°C. The values of a used in these calculations are those which have been found to give the closest fit between theoretical and observed values of activity coefficients, (Harned and Owen, 1950), and of osmotic coefficients, (Falkenhagen, 1934). Since a_i is assumed to be equal to a_-, $\lambda_+ = \lambda_-$ in the case of the uni-univalent electrolytes. In the case of unsymmetrical electrolytes, where $Z_+ \neq Z_-$, the tabulated values of $Z_j\lambda_i$ correspond to the lower value of Z_j for obvious reasons.

TABLE I

	a(Å)	.001m	.01m	.1m
NaCl	(*a*) 4 02	1 704	1 568	1.252
	(*b*) 4.4	1.586	1.417	1 112
KCl	(*a*) 3.76	1.827	1.689	1.364
	(*b*) 4.10	1.669	1 533	1.22
HCl	(*b*) 5.6	1 204	1.08	·805 *
K_2SO_4	K_+ (*a*) 2.69	2.528	2.30	1.787
	SO_4^{--}	5.056	4.600	3·574
$La(NO_3)_3$	La^{+++} (*a*) 4.97	3.822	3.076	1.901
	NO_3^-	1.274	1.025	.634*

Table I shows that expept in two cases (marked with asterisk), the condition for the validity of the above approximation is not satisfied, and that it is especially so in the case of polyvalent ions or ions of small radius. This latter fact has already been mentioned by Müller (1927). Further λa, is seen to increase with dilution, which is also evident from equation (3). Thus the approximation becomes less justified in dilute solutions.

Gronwall (1928) has pointed out some other inconsistencies of the Debye Hückel theory, but has failed to notice the above simple one.

Recently Bagchi (1950) has obtained a better fit between the calculated and the experimental values of activity coefficients by replacing Boltzmann's distribution in the Debye Hückel theory, by a new distribution fuction which has subsequently been supported theoretically. (Dutta and Bagchi, 1950; Dutta, 1947). The Poisson equation in this case reduces to (for a single electrolyte in solution, giving two sorts of ions) :

$$\nabla^2\lambda_+ = \frac{4\pi\epsilon}{DkT} Z_+Z_- \left[Z_+ e^{Z_+\lambda_+ + Z_-} \quad Z_- e^{-Z_-\lambda_+ + Z_+} \right] n_+ + n_- \ldots \quad (4)$$

where, ψ_+ = potential round the central positive ion,

$\lambda_+ = \frac{e\psi_+}{kT}$, and n_+, n_-, Z_+, Z_-, D, k and T have the same significance as in Debye's theory.

Bagchi has solved the above equation (4) by approximating in the following way :

(*i*) for $\lambda_+ \simeq o$, equation (4) reduces to :

$$\nabla^2\lambda_+ = K^2\lambda_+ \qquad (5a)$$

where, $$K^2 = \frac{4\pi\epsilon^2}{DkT} \cdot \frac{Z_+Z_-(Z_+^2 + Z_-^2)}{(Z_+ + Z_-)^2} (n_+ + n_-)$$

with the solution :

$$\lambda_{+(1)} = B\frac{e^{-\xi}}{\xi} \quad \ldots (5)$$

where $\xi = Kr$

and (*ii*) for $\lambda_+ \simeq \infty$, the equation (4) reduces to :

$$\nabla^2\lambda_+ = K^2 m_+ \qquad (6a)$$

where,

$$m_+ = \frac{(Z_+ + Z_-)^2}{Z_+(Z_+ + Z_-^2)}$$

with the solution :

$$\lambda_{+(2)} = m_+\left[\frac{\xi^2}{6} + C + \frac{H}{\xi}\right] \qquad (6)$$

The constants B, C and H have been determined by fiittng the two solutions (5) and (6) togethei on the surface $\lambda_+ = m_+$ so that (5) should hold for $\lambda_+ < m_+$ and (6) for $\lambda_+ > m_+$.

The electrical free energy has been calculated after Debye ; thus, here also, only the surface potential of the central ion is significant. Since however, Bagchi has used only the second solution in calculating the free energy, it is evident that we should have $(\lambda_{i(2)})r=a_i > m_i$; $i = +, -$.

This has been tested in Table II, by calculating $(\lambda_{i(2)})a_i$ by means of equation (6) for different ions, at different concentrations (molar) and at 25°C. The values of a_i used in the calculations are the same as those used by Bagchi for calculating the activity coefficients. The univalent ions are supposed to be derived from uni-univalent electrolytes. The values of m_i are also included for comparision.

TABLE II

	a_i (Å)	m_i	.01 m	1 m	4 m
K^+	1.33	2	5.204	4.146	3.367
	2.76	,,	2.428	1.587 *	1.244 *
Rb_+	1.48	,,	4.66	3.62	2.88
Cs^+	1.67	,,	4.113	3.097	2.411
Cl^-	1.81	,,	3.78	2.787	2.141
Br_-	1.96	,,	3.481	2.505	1.906 *
I^-	2.19	,,	3.10	2.16	1.626 *
Na^+	3.2	,,	2.071	1.303 *	1.03 *
Na^+, H^+,Cl^-	5	,,	1.28 *	.83 *	.828 *
$BaCl_2$ Ba^{++}	1.31	.9	10.405	8.019	6.4
Cl^-	1.81	1.8	3.665	2.239	1.56 *
$LaCl_3$ La^{+++}	1.06	.533	19.33	15.71	13.03
Cl^-	1.81	1.6	3.54	1.83	1.22 *

From Table II it is clear that the assumption $(\lambda_{i(2)})a_i > m_i$ is justified in most cases, and that most of the cases where it does not hold (marked with an asterisk) are those where Bagchi has taken large artificial values for the ionic radii to get a closer fit between the calculated and the experimental values of activity coefficients.

Thus it is clear that at least with respect to the consistency of method, as put forward in this note, the calculations of Bagchi are more satisfactory than those of Debye and Hückel.

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